

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 79301675.9

(51) Int. Cl.³: C 08 G 65/48

(22) Date of filing: 16.08.79

C 08 G 61/12, C 08 G 75/23

(30) Priority: 05.09.78 GB 7835589
24.01.79 GB 7802490

(71) Applicant: IMPERIAL CHEMICAL INDUSTRIES LIMITED
Imperial Chemical House Millbank
London SW1P 3JF(GB)

(43) Date of publication of application:
19.03.80 Bulletin 80/6

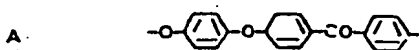
(72) Inventor: Rose, John Brewster
"Uluvia" Pasture Road
Letchworth, Hertfordshire(GB)

(84) Designated Contracting States:
DE FR GB

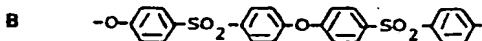
(74) Representative: Sheller, Alan et al,
Imperial Chemical Industries Limited Legal Department:
Patents Thames House North Millbank
London SW1P 4QG(GB)

(54) Sulphonated polyaryletherketones and process for the manufacture thereof.

(57) A polyaryletherketone polymer which is a hydrophilic sulphonated polymer derived by controllably sulphonating a polymer having the repeat unit of formula



alone or in conjunction with the repeat unit of formula



the latter units, if present, remaining substantially non-sulphonated after sulphonation. The sulphonation may be effected using 98 % w/w concentrated sulphuric acid.

EP 0 008 895 A1

BEST AVAILABLE COPY

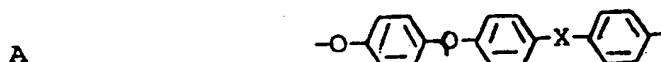
BAD ORIGINAL



SULPHONATED POLYARYLEETHERKETONES

The present invention relates to certain sulphonated polyaryletherketone polymers.

Certain polyarylethers containing the repeat unit of
5 formula

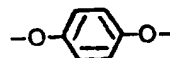


where X is $-SO_2-$ or $-CO-$ have been found to undergo interesting and useful sulphonation reactions in concentrated sulphuric acid (98% w/w). The
10 polyarylethersulphone containing only the repeat unit A in which X is $-SO_2-$ dissolves in the concentrated sulphuric acid and sulphonates very rapidly to give a completely water-soluble product, due to the mono-
15 aromatic rings in the sub-units



of the polymer (see Example 4).

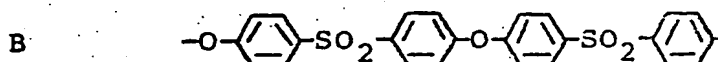
In the case of the polyaryletherketone containing only the repeat unit A in which X is $-CO-$, however,
20 dissolution of the polymer in concentrated sulphuric acid (98% w/w) occurs but monosulphonation of the sub-units



is much slower.

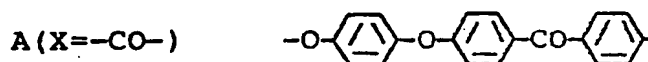
Consequently the degree to which a polymer of repeat
25 unit A in which X is $-CO-$ can be sulphonated may be readily controlled by controlling the conventional factors affecting sulphonation degree in concentrated sulphuric acid, and in particular the time of sulphonation. In this way the hydrophilicity of the resulting sulphonated
30 polymer can be readily controlled.

Additionally, while the sulphonation of polymers containing only the repeat unit A in which X is $-\text{SO}_2-$ is almost instantaneous and cannot be controlled, unlike the case where X is $-\text{CO}-$, polyarylethersulphones containing only the repeat unit of formula



are virtually non-susceptible to sulphonation in concentrated sulphuric acid (98% w/w), the sulphuric acid dissolving the polymer but not changing it (see Example 5), even though other sulphonating agents such as oleum and chlorosulphonic acid, and even a mixture of concentrated sulphuric acid (98% w/w) with a little oleum, completely sulphonate the polymer and/or degrade it (see Examples 6 and 7). Consequently polyaryletherketone/sulphone copolymers containing the repeat unit A in which X is $-\text{CO}-$ and the repeat unit B may also be controllably sulphonated in concentrated sulphuric acid (98% w/w) to give hydrophilic sulphonated copolymers.

According to the present invention there is provided a polyaryletherketone polymer which is a hydrophilic sulphonated polymer derived by controllably sulphonating a polymer having the repeat unit of formula



alone or in conjunction with the repeat unit of formula



the latter units, if present, remaining substantially non-sulphonated after sulphonation.

The extent of the sulphonation in concentrated sulphuric acid (98% w/w) of the units A in which X is $-\text{CO}-$

slows down with increasing time and it may require a very long sulphonation period to obtain a polyaryletherketone according to the invention in which more than 90% of these units are sulphonated.

5 The control of the sulphonation reaction should be such that the resulting polymer preferably has a degree of hydrophilicity corresponding to a water absorption capacity at ambient temperature of about 2 weight % water absorption to complete solubility in water.

10 The hydrophilic polymers of the invention (which preferably absorb 5-75 weight % water at ambient temperature) are potentially useful as membrane materials, e.g. for ultra-filtration processes such as desalination and removal of microorganisms, since they are not only
15 hydrophilic in character but retain considerable strength even when containing a significant quantity of water (e.g. up to 20 weight % water).

 Ionomers of the above-defined polymers which are sulphonated with $-SO_2OH$ groups may be readily prepared
20 e.g. by converting the $-SO_2OH$ groups to salts such as SO_3-M^+ (where M = an alkali metal or NR_4 , R being an alkyl group); these too have utility as hydrophilic polymers. Accordingly, the sulphonyl groups on the polymers of the invention preferably have the formula
25 $-SO_2OY$ where Y is H , an alkali metal, or NR_4 where R is an alkyl group.

 A sulphonated polyaryletherketone polymer according to the present invention may also possess further utility in that it may, if used in admixture with a non-
30 sulphonated polymer of repeat unit A in which X is $-CO-$, cause the polymer mixture to undergo cross-linking if heated at a suitable temperature thereby improving certain properties of the non-sulphonated polymer such as softening point and resistance to solvents under stress.

Such a cross-linking technique could usefully be applied to fabricated articles made from non-sulphonated polymers of repeat unit A in which X is -CO- having inherent viscosity (IV) of at least 0.7 (measured at 25°C as 0.1% solution in H₂SO₄ of density 1.84), which have excellent mechanical and electrical properties coupled with outstanding thermal and combustion characteristics and are particularly advantageous when used as insulation for electrical conductors (and in particular as insulating coatings for wires and cables) in that they exhibit high resistance to attack by solvents and to heat stress embrittlement. Cross-linking of such a fabricated article could e.g. be effected by steeping the article in concentrated sulphuric acid, removing the article from the sulphuric acid bath and washing out any non-absorbed sulphuric acid, and then heating the article to cause sulphonation of some of the polymer chains and concomitant cross-linking. This could provide a cross-linked sulphonated article of still further improved properties, particularly in respect of resistance to solvent stress cracking.

Polyaryletherketone polymers of repeat unit A in which X is -CO- alone or in conjunction with repeat unit B and having IV of at least 0.7 may be conveniently prepared by condensation of hydroquinone, 4,4'-difluorobenzophenone and, where units B are present, 4,4'-dihydroxydiphenylsulphone, and an alkali metal carbonate or bicarbonate in the presence of an aromatic sulphone solvent at 150-400°C - as described in our European Patent Publication No. 0 001 879.

The present invention is now illustrated by the following examples.

EXAMPLE 1

A homopolymer of repeat unit A in which X is -CO- (20 g), (IV 1.0), was shaken for 18 hours with concentrated

5 sulphuric acid (98% w/w) (100 ml) to give a very viscous solution. Next morning further concentrated sulphuric acid (100 ml) was added and shaking continued for a further 6 hours (i.e. 22 hours in all). Some of this solution (50 ml) was then poured into distilled water (500 ml) in a Waring blender to give a white precipitate which was filtered off and then washed three times with further water in the blender, separated each time by filtration. The product was left wet overnight. Next morning the water-wet product was found to be soluble in boiling dimethyl formamide and in boiling dimethyl sulphoxide and did not precipitate on cooling. Analysis by 220 MHz nuclear-magnetic-resonance (nmr) spectroscopy of a solution in dimethyl sulphoxide showed that 35% of the repeat units bore $-SO_2OH$ groups.

10 Further portions of the homopolymer of repeat unit A in which X is $-CO-$ were similarly sulphonated by shaking in concentrated sulphuric acid (98% w/w) for periods of 3 hours, 46 hours, 10 weeks and 11 weeks. The products had the following properties:

20 3 hours

Insoluble in dimethyl sulphoxide (and therefore not analysed by nmr).

46 hours

56% of repeat units bore an $-SO_2OH$ group, actually determined on the sodium salt, which was precipitated by adding the sulphonation solution to 10 volumes of sodium hydroxide solution (5 weight %) in water, and was soluble in dimethyl sulphoxide.

25 10 weeks

89% of repeat units bore an $-SO_2OH$ group. Product was soluble in water but precipitated by 5% sulphuric acid in water.

11 weeks

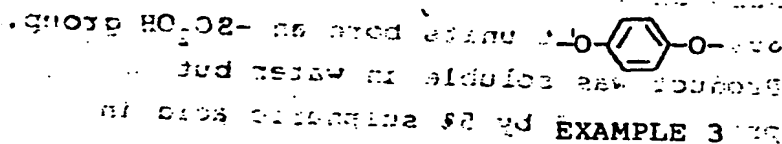
90% of repeat units bore an $-SO_2OH$ group.

EXAMPLE 2

A homopolymer of repeat unit A in which X is -CO- (20 g), (IV 1.0), was dropped into stirred concentrated sulphuric acid (98% w/w) (500 ml) and the mixture shaken from time to time during the next few hours to help dissolve the polymer. Samples of the solution (50 ml) were withdrawn at various times and precipitated each time by pouring the acid solution into distilled water (500 ml) in a Waring blender to give a precipitate which was filtered off, reslurried in distilled water in the blender, separated by filtration and washed twice with water. The product samples corresponding to the various times of sulphonation were analysed by 220 MHz nmr spectroscopy as solutions in dimethyl sulphoxide and found to have the following properties:

<u>1 hour</u>	Not analysed as insoluble in dimethyl sulphoxide.
<u>2 hours</u>	Not analysed as insoluble in dimethyl sulphoxide.
<u>3.5 hours</u>	Not analysed as insoluble in dimethyl sulphoxide.
<u>7 hours</u>	43% of repeat units bore an -SO ₂ OH group.
<u>23 hours</u>	62% of repeat units bore an -SO ₂ OH group.
<u>31 hours</u>	75% of repeat units bore an -SO ₂ OH group.
<u>48 hours</u>	83% of repeat units bore an -SO ₂ OH group.

All the sulphonated repeat units appeared to be mono-sulphonated on the sub-repeat units



The water absorption of the polymers of Example 2 that had been sulphonated for 23 hours, 31 hours and 48 hours respectively were measured after steeping initially dry films of the polymers (cast from solution in

dimethylformamide) in water for 24 hours at ambient temperature. The values obtained were 24 weight %, 59 weight % and 70 weight % respectively.

EXAMPLE 4

- 5 A homopolymer of repeat unit A in which X is $-\text{SO}_2-$ (10 g) was dissolved in concentrated sulphuric acid (98% w/w) with stirring and samples (50 ml) removed from time to time and precipitated into saturated sodium sulphate or dilute sulphuric acid; the polymer samples corresponding
- 10 to the various times of sulphonation were analysed by 220 MHz nmr spectroscopy as solutions in dimethylsulphoxide and found to have the following properties:

- | | |
|-------------------|---|
| <u>1 hour</u> | 85% of the units bore an $-\text{SO}_2\text{OH}$ group (isolated as Na salt). |
| 15 <u>2 hours</u> | 99% of the units bore an $-\text{SO}_2\text{OH}$ group (isolated as Na salt). |
| <u>4.5 hours</u> | 100% of the units bore an $-\text{SO}_2\text{OH}$ group (isolated as Na salt). |
| <u>23 hours</u> | 98% of the units bore an $-\text{SO}_2\text{OH}$ group (isolated as free acid). |
| 20 | Substantially all the sub-units bore one $-\text{SO}_2\text{OH}$ group. |

EXAMPLE 5

- A homopolymer containing the repeat unit B (50 g) was dissolved in concentrated sulphuric acid (98% w/w)
- 25 (200 ml), left for 72 hours, precipitated in dilute sulphuric acid, washed, macerated and dried. The infrared and nmr spectra of the product showed it to be identical with the starting material.

EXAMPLE 6

- 30 A homopolymer containing the repeat unit B (20 g) was added to chlorosulphonic acid (100 ml). Slight effervescence was apparent and white fumes were evolved. After standing overnight (the total time of the polymer in the acid being 20 hours), the solution was poured into
- 35 300 ml of concentrated sulphuric acid (98% w/w) and this

solution then poured onto ice. A very fine precipitate resulted, which filtered very slowly and was washed once with water and then dried. The product appeared to be almost entirely soluble in water indicating a high degree of sulphonation.

EXAMPLE 7

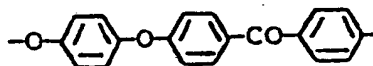
A homopolymer of repeat unit B (20 g) was mixed with oleum (150 ml) and left overnight. The resulting black solution still contained undissolved polymer and so the mixture was stored for a further 5 hours, and then poured into water. No precipitate was obtained, but instead a brownish/orange solution was obtained. The product was discarded, being assumed to be highly sulphonated or entirely degraded.

In another experiment, the homopolymer of repeat unit B (15 g) was dissolved in concentrated sulphuric acid (98% w/w); oleum (50 ml) was then added and the solution stirred for 30 minutes and then poured onto ice and left overnight. A rubbery white solid was precipitated and was washed and dried. This product was found to be highly sulphonated.

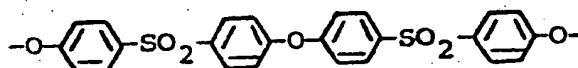
CLAIMS

1. A polyaryletherketone polymer which is a hydrophilic sulphonated polymer derived by controllably sulphonating a polymer having the repeat unit of formula

5



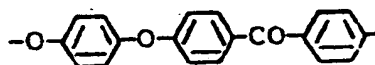
alone or in conjunction with the repeat unit of formula



the latter units, if present, remaining substantially non-sulphonated after sulphonation.

10

2. A polyaryletherketone polymer according to claim 1 in which $\leq 90\%$ of the units

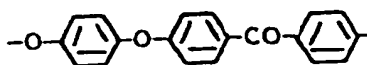


in the polymer are sulphonated.

3. A polyaryletherketone polymer according to either claim 1 or claim 2 having a hydrophilicity corresponding to a water adsorption capacity at ambient temperature of 2 weight % water absorption to complete solubility in water.

4. A polyaryletherketone polymer according to claim 3 having a hydrophilicity corresponding to a water absorption capacity at ambient temperature of 5 to 75 weight %.

5. A polyaryletherketone polymer according to any one of the preceding claims derived by controllably sulphonating a polymer having the repeat unit



only.

6. A polyaryletherketone polymer according to any one of the preceding claims having inherent viscosity IV of at least 0.7.

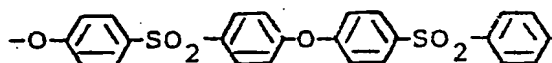
7. A polyaryletherketone polymer according to any one of the preceding claims in which the sulphonyl groups on the polymer have the formula $-\text{SO}_2\text{OY}$ where Y is H, an alkali metal, or NR_4 where R is an alkyl group.

8. A polyaryletherketone polymer according to any one of the preceding claims in the form of a film or electrical insulation.

9. A process for the production of a hydrophilic sulphonated polyaryletherketone polymer which comprises controllably sulphonating using concentrated sulphuric acid (98% w/w) a polymer having the repeat unit of formula



alone or in conjunction with the repeat unit of formula



to produce a sulphonated polymer in which the latter units, if present, are substantially non-sulphonated.

10. A process according to claim 9 wherein $\leq 90\%$ of the units



are sulphonated.

PALS78341500/RJ



European Patent
Office

EUROPEAN SEARCH REPORT

0008895

Application number

EP 79 301 675.9

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<p>US - A - 3 709 841 (J.P. QUENTIN)</p> <p>* claims 1, 7; column 2, lines 3 to 17 and line 27 *</p>	1,8,9	<p>C 08 G 65/48</p> <p>C 08 G 61/12</p> <p>C 08 G 75/23</p>
A	<p>US - A - 4 054 707 (J.P. QUENTIN)</p> <p>* claims 1, 4; column 1, line 64 to column 2, line 5 *</p>	7,9	
A	<p>GB - B - 1 078 234 (UNION CARBIDE)</p> <p>* claims 1, 4, 6 *</p>		<p>TECHNICAL FIELDS SEARCHED (Int. Cl.)</p> <p>C 08 G 61/00</p> <p>C 08 G 65/00</p> <p>C 08 G 75/00</p> <p>C 08 G 85/00</p> <p>C 08 J 7/00</p> <p>C 08 L 65/00</p> <p>C 08 L 71/00</p> <p>C 08 L 81/00</p>
A	<p>W. FOERST "Ullmanns Encyklopädie der technischen Chemie"</p> <p>3rd edition, vol. 14,</p> <p>1963 URBAN AND SCHWARZENBERG, München, Berlin</p> <p>* pages 595 to 597 *</p>		
A	<p>R.T. MORRISON et al. "Lehrbuch der organischen Chemie"</p> <p>1974 VERLAG CHEMIE, Weinheim/Bergstr.</p> <p>* page 398 *</p>		<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant</p> <p>A: technological background</p> <p>O: non-written disclosure</p> <p>P: intermediate document</p> <p>T: theory or principle underlying the invention</p> <p>E: conflicting application</p> <p>D: document cited in the application</p> <p>L: citation for other reasons</p>
<p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p>			<p>&: member of the same patent family, corresponding document</p>
<p>Place of search</p> <p>Berlin</p>		<p>Date of completion of the search</p> <p>04-12-1979</p>	<p>Examiner</p> <p>MARX</p>

EPO Form 1503.1 06.78

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)